Bäcklund flux-quantization in a model of electrodiffusion based on Painlevé II

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Abstract

A previously-established model of steady one-dimensional two-ion electrodiffusion across a liquid junction is reconsidered. It involves three coupled first-order nonlinear ordinary differential equations, and has the second-order Painlevé II equation at its core. Solutions are now grouped by Bäcklund transformations into infinite sequences, partially labelled by two Bäcklund invariants. Each sequence is characterized by evenly-spaced quantized fluxes of the two ionic species, and hence evenly-spaced quantization of the electric current-density. Finite subsequences of exact solutions are identified, with positive ionic

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concentrations and quantized fluxes, starting from a solution with zero electric field found by Planck, and suggesting an interpretation as a ground state plus excited states of the system. Positivity of ionic concentrations is established whenever Planck's charge-neutral boundary-conditions apply. Exact solutions are obtained for the electric field and ionic concentrations in well-stirred reservoirs outside each face of the junction, enabling the formulation of more realistic boundary-conditions. In an approximate form, these lead to radiation boundary conditions for Painlevé II. Illustrative numerical solutions are presented, and the problem of establishing compatibility of boundary conditions with the structure of flux-quantizing sequences is discussed.

1 Introduction

Transport of charged ions across liquid junctions plays a fundamental role in a variety of important physical and biological contexts, in particular semiconductor theory, electrochemistry and models of the nervous system. Many years ago, an extension of the Nernst-Planck model of ion transport [1, 2] was proposed [3, 4, 5], incorporating the effect of the electric field that develops within the junction in response to charge separation. Such separation tends to develop as ions diffuse with different diffusion coefficients, while the consequent electric field acts to inhibit it. This feedback leads to nonlinearity of the extended model.

Mathematically, the extension involves the use of Gauss' Law to relate charge density to electric field, together with the imposition of Einstein's relation between diffusivities and mobilities of the ions. In its simplest form, the model deals with one-dimensional transport across an infinite slab occupying $0 \leq x \leq \delta$, for two types of ions carrying equal and opposite charges. With the concentrations of the two ionic species and the induced electric field within the slab denoted by $c_{\pm}(x)$ and $E(x)$ respectively, the governing system of coupled ordinary differential equations (ODEs) obtained is

$$c_+{}'(x) = (\tilde{z}e/k_BT)\, E(x)\, c_+(x) - \Phi_+/D_+\,,$$

$$c_-{}'(x) = -(\tilde{z}e/k_BT)\, E(x)\, c_-(x) - \Phi_-/D_-\,,$$

$$E\,'(x) = (4\pi\tilde{z}e/\epsilon)\, [c_+(x) - c_-(x)] \tag{1}$$

for $0 < x < \delta$. Here Φ_+ and Φ_- denote the steady (constant) fluxes of the two species in the x-direction across the slab, $\tilde{z}$ their common valence, and $D_{\pm}$ the corresponding diffusion constants, while k_B denotes Boltzmann's constant, e the electronic charge, and T the ambient absolute temperature within the solution in the slab. An important auxiliary quantity is the electric current-density

$$J = \tilde{z}e\, (\Phi_+ - \Phi_-)\,. \tag{2}$$

The slab equations (1) when supplemented by two-point boundary conditions (BCs) specify the electrical structure of liquid junctions including nerve membranes. The latter are so thin (of the order of $10^{-6}\,cm$) that typical physiological potential differences of $0.1\,V$ generate large fields of order $10^5\,V/cm$. In that context it is not only the potential difference across the slab (which was of primary interest to Nernst [1] and Planck [2]) but the electric field distribution within it that may be important [6].

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In a special case when $\Phi_- = 0$, it was shown [3] that as a consequence of (1), $c_-(x)$ satisfies a second order nonlinear equation that can be transformed into the Painlevé II ODE (PII). Independently, it was shown [4] that in the general case, and with 2-point BCs, the field $E(x)$ also satisfies a form of PII (see (13) below). These were perhaps the first applications of PII to physics or biology. Since the introduction of the model defined by (1), this aspect and others have been much studied (see [7, 8, 9] and references therein). In particular, more recent analysis [10, 11] has drawn attention to the relevance to the model of already-known exact solutions of PII, and of Bäcklund transformations [12] of its solutions more generally.

In the formulation given in [4], the model equations (1) were supplemented by BCs corresponding to charge-neutrality at each face of the slab, so that $c_+(0) = c_-(0)$ and $c_+(\delta) = c_-(\delta)$. From (1), these imply that $E'(0) = 0 = E'(\delta)$, and hence lead to BCs of Neumann type for PII as it appears in (13) below). We shall discuss the relevance of these BCs, and the possibility of imposing others corresponding to the presence of well-stirred ionic reservoir solutions outside the membrane slab, occupying $-\infty < x < 0$ and $\delta < x < \infty$. We shall also downplay the role of PII, emphasized in previous analyses of the model, in part because of the peculiar feature that boundary values of $E(x)$ appear in the coefficients of that ODE for $E(x)$ itself, as it appears in the form (13). This complicates its theoretical and numerical analysis [13, 14]. In contrast, we find that the system (1) is solved numerically with no difficulty by commercial packages such as MAPLE [15], at least in cases corresponding to charge-neutrality at $x = 0$ and $x = \delta$. (See Sec. 6.1.)

By working directly with the system (1), we also avoid singling out the electric field, and give comparable weight to the ionic concentrations, and their associated fluxes. This will enable us to elucidate the role of Bäcklund transformations in producing sequences of solutions of (1) in which the fluxes are quantized.

Of particular interest are finite subsequences of exact solutions with positive concentrations, generated by Bäcklund transformations from a solution of (1), first written down by Planck [2], with $c_+(x) = c_-(x)$ and $E(x) = 0$ throughout the junction. It is remarkable that Planck's solution, obtained by him when modelling electrodiffusion 10 years before his fundamental work on quantization of black-body radiation, should now appear some 120 years later as the seed solution in sequences exhibiting Bäcklund flux-quantization.

As we shall see, there are difficulties reconciling either of the two kinds of BCs mentioned above, with the formation of such sequences of solutions. This raises the problem of identifying what form of BCs if any is consistent with 'Bäcklund flux-quantization.'

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2 Preliminary remarks and Painlevé II

With the introduction of a suitable constant reference concentration $c_{ref.}$, to be identified later, and with the change to dimensionless independent and dependent variables

$$x^* = x/\delta \,, \quad c_\pm^*(x^*) = c_\pm(x)/c_{ref.} \,,$$

$$E^*(x^*) = (\tilde{z}e\delta/k_B T)\, E(x) \,, \tag{3}$$

and dimensionless constants

$$A_\pm = -\Phi_\pm \delta/c_{ref.} D_\pm \,, \quad \lambda = \sqrt{\epsilon k_B T/4\pi(\tilde{z}e)^2 \delta^2\, c_{ref.}} \tag{4}$$

the equations (1) become (on immediately dropping all the asterisks)

$$c_+{}'(x) = E(x)\, c_+(x) + A_+ \,,$$

$$c_-{}'(x) = -E(x)\, c_-(x) + A_- \,,$$

$$\lambda^2 E\,'(x) = c_+(x) - c_-(x) \tag{5}$$

for $0 < x < 1$. The current density is also conveniently made dimensionless by setting

$$j = \frac{\delta}{(\tilde{z}e)c_{ref.}(D_+ + D_-)}\, J \,. \tag{6}$$

In terms entirely of dimensionless quantities we then have

$$j = \alpha_- A_- - \alpha_+ A_+ \,, \tag{7}$$

where

$$\alpha_\pm = D_\pm/(D_+ + D_-) \ \ (\text{so that } \alpha_\pm > 0 \text{ and } \alpha_+ + \alpha_- = 1)\,. \tag{8}$$

After the first two of (5) are added, and the third is applied, one integration can be performed to deduce that

$$P(x) - \theta x = B \quad (\text{const.})\,, \tag{9}$$

where

$$P(x) = c_+(x) + c_-(x) - \tfrac{1}{2}\lambda^2 E(x)^2 \,, \quad \theta = A_+ + A_- \,. \tag{10}$$

Eq. (9) has the general meaning of a work-energy relation. This can be seen by returning to the original variables for the moment and multiplying through by $k_B T$, to obtain the result

$$k_B T[c_+(x) + c_-(x)] - \epsilon E(x)^2/8\pi - [\Phi_+/u_+ + \Phi_-/u_-]x = \text{const.} \qquad (11)$$

where $u_+ = D_+/k_B T$ and $u_- = D_-/k_B T$ are the mobilities of the two types of ions. Here $k_B T[c_+(x) + c_-(x)] - \epsilon E(x)^2/8\pi$ is the ionic (osmotic) pressure at x in the presence of the electric field. The minus sign reflects the fact that the electric field tends to keep the oppositely charged ions together, effectively reducing their degrees of freedom and hence the associated pressure. The term $[\Phi_+/u_+]x$ (resp. $[\Phi_-/u_-]x$) is the work done per unit volume against the resistance offered by the background fluid, in transporting positive (resp. negative) ions from 0 to x. Accordingly, we may refer to $P(x)$ and θ as (the dimensionless forms of) the pressure at x, and the resistive force-density, respectively.

Differentiating the third of (5) once and then applying the first two of (5) to eliminate $c_+{}'(x)$ and $c_-{}'(x)$ from the result, leads to

$$\lambda^2 E''(x) = E(x)\left[c_+(x) + c_-(x)\right] + (A_+ - A_-) \qquad (12)$$

and, with the help of (9) to

$$\lambda^2 E''(x) - \tfrac{1}{2}\lambda^2 E(x)^3 - (\theta x + B)E(x) - (A_+ - A_-) = 0\,. \qquad (13)$$

This can be brought to a standard form of PII by a constant scaling of the dependent variable, together with a linear transformation of the independent variable [4, 11].

From any solution $E(x)$ of (13), corresponding $c_\pm(x)$ can be obtained using (9) and the third of (5). In this way, PII determines all solutions of (5). The results of many studies [10]-[14], [16]-[24] of PII can then be brought to bear on the problem of interest, in particular Bäcklund transformations and exact solutions. These have been extensively explored elsewhere [11] in the context of electrodiffusion on a half line rather than a finite interval of the x-axis, which is our focus here.

3 Planck's solution

Planck [2] considered the situation where λ is vanishingly small. As (4) shows, this occurs when the electric charges $\pm\tilde{z}e$ are much larger in magnitude than $\sqrt{\epsilon k_B T/4\pi\delta^2\,c_{ref.}}$. (Here the choice of $c_{ref.}$ becomes relevant — see the

Remark following (67) below.) In the limit $\lambda \to 0$, with $c(0) = c_0$, the system (5) is easily solved to give Planck's solution

$$c_+(x) = c_-(x) = c(x) = c_0 + \tfrac{1}{2}(A_+ + A_-)x\,,$$

$$E(x) = \tfrac{1}{2}(A_- - A_+)/c(x)\,. \tag{14}$$

With the help of (2) the electric field may also be written as [5]

$$E(x) = \frac{j}{c(x)} + \frac{(\alpha_+ - \alpha_-)(c_1 - c_0)}{c(x)}\,, \tag{15}$$

where $c_1 = c(1) = c_0 + (A_+ + A_-)/2$, which brings to the fore the role of the electric current density: the first term on the RHS of (15) is the ohmic contribution to the field, and the second term is the gradient of the Nernst-Planck potential [2]. The situation where $j = 0$ is of particular physical interest.

For any value of j, Planck's solution (14) might be used as the zeroth-order term in an asymptotic expansion, in powers of λ^2, of a solution to the system (5) with $\lambda \neq 0$. This would require the methods of singular perturbation theory, as is clear from the way in which λ^2 appears multiplying the highest derivative in (13). That approach has been developed previously for closely related problems [25, 26], and will not be pursued here.

For our purposes in what follows, it is more important to note that (14) defines an exact solution of the full system (5) in the special case that $A_+ = A_- = c_1 - c_0$ and hence $E(x) \equiv 0$. This solution, which has $j \neq 0$, plays the role of the seed for an infinite sequence of exact rational solutions [18, 19, 21, 22, 10, 11] generated by Bäcklund transformations, as highlighted in Sec. 6 below.

4   A discrete symmetry group

The system (5) must be supplemented by appropriate BCs, as we discuss below, to determine physically meaningful solutions with nonsingular $c_\pm(x)$, positive on $[0,1]$. For the time being we ignore such considerations. Bearing in mind the way that PII determines all solutions of (5), and that solutions of PII itself, when regarded as analytic functions, may have (movable) simple poles, we mean by "a solution $\mathcal{S} = (c_+\,, c_-\,, E\,, A_+\,, A_-)$", any two real constants A_+, A_-, together with any three real-valued functions c_+, c_-, E satisfying (5) almost everywhere on $[0,1]$.

Given one solution $\mathcal{S} = (c_+, c_-, E, A_+, A_-)$, straightforward if sometimes lengthy manipulations confirm that in general there exist four other solutions. These transformed solutions can be found from known symmetries of PII [11], but they are presented together here, in terms of the variables of the system (5), for the first time. The transformed solutions, each of which we denote by $\hat{\mathcal{S}} = (\hat{c}_+, \hat{c}_-, \hat{E}, \hat{A}_+, \hat{A}_-)$ in turn, are as follows :—

4.1 Conjugate solution

Here $\hat{\mathcal{S}} = \mathcal{C}(\mathcal{S})$, where

$$\hat{c}_+ = c_-\,, \quad \hat{c}_- = c_+\,, \quad \hat{E} = -E\,, \quad \hat{A}_+ = A_-\,, \quad \hat{A}_- = A_+\,. \tag{16}$$

Noting that a second application of $\mathcal{C}$ returns $\hat{\mathcal{S}}$ to the starting solution $\mathcal{S}$, we write

$$\mathcal{C}^2 = I\,. \tag{17}$$

4.2 Reflected solution

Here $\hat{\mathcal{S}} = \mathcal{R}(\mathcal{S})$, where

$$\hat{c}_+(x) = c_+(1-x)\,, \quad \hat{c}_-(x) = c_-(1-x)\,,$$

$$\hat{E}(x) = -E(1-x)\,, \quad \hat{A}_+ = -A_+\,, \quad \hat{A}_- = -A_-\,. \tag{18}$$

We note that

$$\mathcal{R}^2 = I\,, \quad \mathcal{R}\mathcal{C} = \mathcal{C}\mathcal{R}\,. \tag{19}$$

4.3 Bäcklund-transformed solution

Here $\hat{\mathcal{S}} = \mathcal{B}(\mathcal{S})$, where

$$\hat{c}_+ = c_- + 2\lambda^2 A_+ E/c_+ + 2\lambda^2 A_+^2/c_+^2\,, \quad \hat{c}_- = c_+\,,$$

$$\hat{E} = -E - 2A_+/c_+\,, \quad \hat{A}_+ = 2A_+ + A_-\,, \quad \hat{A}_- = -A_+\,. \tag{20}$$

We note that if $A_+ = 0$, then $\mathcal{B}(S) = \mathcal{C}(S)$.

4.4   Inverse Bäcklund-transformed solution

Here $\hat{\mathcal{S}} = \mathcal{B}^{-1}(\mathcal{S})$, where

$$\hat{c}_+ = c_- , \quad \hat{c}_- = c_+ - 2\lambda^2 A_- E/c_- + 2\lambda^2 A_-^2/c_-^2 ,$$

$$\hat{E} = -E + 2A_-/c_- , \quad \hat{A}_+ = -A_- , \quad \hat{A}_- = 2A_- + A_+ . \tag{21}$$

We note that if $A_- = 0$, then $\mathcal{B}^{-1}(\mathcal{S}) = \mathcal{C}(\mathcal{S})$.

It is straightforward to check that $\mathcal{B}^{-1}$ is indeed inverse to $\mathcal{B}$, and we write

$$\mathcal{B}^{-1}\mathcal{B} = I = \mathcal{B}\mathcal{B}^{-1} . \tag{22}$$

It is also easily checked that

$$\mathcal{C}\mathcal{B} = \mathcal{B}^{-1}\mathcal{C} , \quad \mathcal{R}\mathcal{B} = \mathcal{B}\mathcal{R} , \quad \mathcal{R}\mathcal{B}^{-1} = \mathcal{B}^{-1}\mathcal{R} . \tag{23}$$

From (23), (19) and (17), it then follows that $\mathcal{C}$, $\mathcal{R}$ and $\mathcal{B}$, together with their inverses and with I as unit, generate a discrete invariance group of transformations of the system (5). Except on special solutions, this group is of infinite order.

From (16), (20) and (21), it is also easily seen that the quantities $P(x)$ (pressure at x) and θ (resistive force density) as in (9) and (10) are invariant under the action of the subgroup generated by $\mathcal{C}$, $\mathcal{B}$ and $\mathcal{B}^{-1}$. It is unclear why these physical quantities should be singled out to be invariants. The invariant θ plays a central role in flux-quantization below.

4.5   Gambier-transformed solutions

There also exist invertible transformations, which we call Gambier and inverse Gambier transformations, that carry solutions back and forth between two special subclasses. These subclasses are of particular interest because one contains, among others, exact solutions of rational type, while the other contains, among others, exact solutions of Airy type [11]. These transformations and their inverses, to be denoted by $\mathcal{G}_\pm$ and $\mathcal{G}_\pm^{(-1)}$ respectively, and to be defined in what follows, can also be derived from a known (restricted) symmetry of PII discovered by Gambier [17, 23, 24]. We present them explicitly here in terms of the variables in (5) for the first time, as follows.

The transformation $\mathcal{G}_+$ (resp. $\mathcal{G}_-$) converts any solution $\mathcal{S}$ in which $A_+ = 0$ (resp. $A_- = 0$), into a solution $\hat{\mathcal{S}}$ in which $\hat{A}_+ = \hat{A}_-$. If $\mathcal{S}$ has the value B

for the first-integral in (9), then $\hat{\mathcal{S}}$ has corresponding value $\hat{B} = -B/2$. In detail, if $A_+ = 0$ and $A_- = A$, the transformed solution $\hat{\mathcal{S}} = \mathcal{G}_+(\mathcal{S})$ has

$$\hat{c}_+(x) = \tfrac{1}{4}\lambda E(x)\sqrt{2c_+(x)} + \tfrac{1}{2}c_+(x) - \tfrac{1}{4}(Ax + B),$$

$$\hat{c}_-(x) = -\tfrac{1}{4}\lambda E(x)\sqrt{2c_+(x)} + \tfrac{1}{2}c_+(x) - \tfrac{1}{4}(Ax + B),$$

$$\hat{E}(x) = \sqrt{2c_+(x)}/\lambda, \quad \hat{A}_+ = \hat{A}_- = -\tfrac{1}{4}A, \quad \hat{B} = -\tfrac{1}{2}B. \tag{24}$$

Similarly, if $A_- = 0$ and $A_+ = A$, the transformed solution $\mathcal{G}_-(\mathcal{S})$ has

$$\hat{c}_+(x) = -\tfrac{1}{4}\lambda E(x)\sqrt{2c_-(x)} + \tfrac{1}{2}c_-(x) - \tfrac{1}{4}(Ax + B),$$

$$\hat{c}_-(x) = \tfrac{1}{4}\lambda E(x)\sqrt{2c_-(x)} + \tfrac{1}{2}c_-(x) - \tfrac{1}{4}(Ax + B),$$

$$\hat{E}(x) = \sqrt{2c_-(x)}/\lambda, \quad \hat{A}_+ = \hat{A}_- = -\tfrac{1}{4}A, \quad \hat{B} = -\tfrac{1}{2}B. \tag{25}$$

4.6 Inverse Gambier-transformed solutions

These convert any solution $\mathcal{S}$ for which $A_+ = A_- = A$, with a given value of B, into solutions with $\hat{A}_+ = 0$ (resp. $\hat{A}_- = 0$) and with $\hat{B} = -2B$. In detail, $\hat{\mathcal{S}} = \mathcal{G}_+^{-1}(\mathcal{S})$ has

$$\hat{c}_+(x) = \tfrac{1}{2}\lambda^2 E(x)^2, \quad \hat{E}(x) = 2(c_+(x) - c_-(x))/\lambda^2 E(x),$$

$$\hat{c}_-(x) = -\tfrac{1}{2}\lambda^2 E(x)^2 + 2(c_+(x) - c_-(x))^2/\lambda^2 E(x)^2 - 4Ax - 2B,$$

$$\hat{A}_+ = 0, \quad \hat{A}_- = -4A, \quad \hat{B} = -2B. \tag{26}$$

and similarly, $\mathcal{G}_-^{-1}(\mathcal{S})$ has

$$\hat{c}_-(x) = \tfrac{1}{2}\lambda^2 E(x)^2, \quad \hat{E}(x) = -2(c_+(x) - c_-(x))/\lambda^2 E(x),$$

$$\hat{c}_+(x) = -\tfrac{1}{2}\lambda^2 E(x)^2 + 2(c_+(x) - c_-(x))^2/\lambda^2 E(x)^2 - 4Ax - 2B,$$

$$\hat{A}_- = 0, \quad \hat{A}_+ = -4A, \quad \hat{B} = -2B. \tag{27}$$

The case when $E(x) \equiv 0$ needs special treatment (see Appendix A). Note that

$$\mathcal{G}_-^{-1}(\mathcal{S}) = \mathcal{C}\mathcal{G}_+^{-1}(\mathcal{S}). \tag{28}$$

5 Sequences of solutions

Repeated application of $\mathcal{B}$ and $\mathcal{B}^{-1}$ produces from *any* 'seed' solution $\mathcal{S}$, a sequence $\mathcal{Q}_{\mathcal{S}}$ of solutions that, except in special cases (see below), is doubly infinite. Thus

$$\mathcal{Q}_{\mathcal{S}} = \{\ldots, \mathcal{B}^{-2}(\mathcal{S}), \mathcal{B}^{-1}(\mathcal{S}), \mathcal{S}, \mathcal{B}(\mathcal{S}), \mathcal{B}^2(\mathcal{S}), \ldots\} \tag{29}$$

There is an associated conjugate sequence

$$\mathcal{Q}_{\mathcal{C}(\mathcal{S})} = \{\ldots, \mathcal{B}^{-2}\mathcal{C}(\mathcal{S}), \mathcal{B}^{-1}\mathcal{C}(\mathcal{S}), \mathcal{C}(\mathcal{S}), \mathcal{B}\mathcal{C}(\mathcal{S}), \mathcal{B}^2\mathcal{C}(\mathcal{S}), \ldots\}$$

$$= \mathcal{C}\{\ldots, \mathcal{B}^2(\mathcal{S}), \mathcal{B}(\mathcal{S}), \mathcal{S}, \mathcal{B}^{-1}(\mathcal{S}), \mathcal{B}^{-2}(\mathcal{S}), \ldots\}$$

$$= \mathcal{C}\mathcal{Q}_{\mathcal{S}}^T, \tag{30}$$

where $\mathcal{Q}_{\mathcal{S}}^T$ is the transpose of the sequence $\mathcal{Q}_{\mathcal{S}}$, *i.e.* the sequence obtained from $\mathcal{Q}_{\mathcal{S}}$ by replacing the nth member by the $(-n)$th member, for $n = 0, \pm 1, \pm 2, \ldots$. There is also an associated reflected sequence

$$\mathcal{Q}_{\mathcal{R}(\mathcal{S})} = \{\ldots, \mathcal{B}^{-2}\mathcal{R}(\mathcal{S}), \mathcal{B}^{-1}\mathcal{R}(\mathcal{S}), \mathcal{R}(\mathcal{S}), \mathcal{B}\mathcal{R}(\mathcal{S}), \mathcal{B}^2\mathcal{R}(\mathcal{S}), \ldots\}$$

$$= \mathcal{R}\{\ldots, \mathcal{B}^{-2}(\mathcal{S}), \mathcal{B}^{-1}(\mathcal{S}), \mathcal{S}, \mathcal{B}(\mathcal{S}), \mathcal{B}^2(\mathcal{S}), \ldots\}$$

$$= \mathcal{R}\mathcal{Q}_{\mathcal{S}}. \tag{31}$$

Because the quantities θ and $P(x) - \theta x$ (with value B) are invariant under the action of $\mathcal{C}$, $\mathcal{B}$ and $\mathcal{B}^{-1}$, every solution in $\mathcal{Q}_{\mathcal{S}}$ and $\mathcal{Q}_{\mathcal{C}(\mathcal{S})}$ has the same values for these quantities. On the other hand, in the reflected sequence $\mathcal{Q}_{\mathcal{R}(\mathcal{S})}$, every solution has $\widehat{B} = B + \theta$ and $\widehat{\theta} = -\theta$. In this way, each of the sequences $\mathcal{Q}_{\mathcal{S}}$, $\mathcal{Q}_{\mathcal{C}(\mathcal{S})}$ and $\mathcal{Q}_{\mathcal{R}(\mathcal{S})}$ is *partially* labelled by the values of B and θ.

6 Bäcklund flux-quantization

It follows from (20) and (21) that, if we write for the moment

$$\mathcal{B}^n(\mathcal{S}) = (c_+^{(n)}, c_-^{(n)}, E^{(n)}, A_+^{(n)}, A_-^{(n)}), \quad n \in \{0, \pm 1, \pm 2, \ldots\}, \tag{32}$$

then

$$A_+^{(n)} + A_-^{(n)} = \theta,$$

$$A_+^{(n)} - A_-^{(n)} = A_+^{(0)} - A_-^{(0)} + 2n\theta. \tag{33}$$

Here θ may take any real value. If $\theta \neq 0$, we see from (33) that without loss of generality we can assume for $\mathcal{S}$ that

$$A_+^{(0)} - A_-^{(0)} = \phi, \quad -\theta \leq \phi < \theta, \tag{34}$$

and we then have

$$A_+^{(n)} = (\tfrac{1}{2} + n)\theta + \tfrac{1}{2}\phi,$$

$$A_-^{(n)} = (\tfrac{1}{2} - n)\theta - \tfrac{1}{2}\phi, \quad n \in \{0, \pm 1, \pm 2, \dots\}. \tag{35}$$

It follows that the steady ionic fluxes as in (1) are also quantized in each of the sequences of solutions generated by Bäcklund transformations and their inverses, with values for the n–th element of the sequence given by

$$\Phi_+^{(n)} = (n+1)\Phi_+^{(0)} + n(D_+/D_-)\Phi_-^{(0)},$$

$$\Phi_-^{(n)} = -(n-1)\Phi_-^{(0)} - n(D_-/D_+)\Phi_+^{(0)}, \tag{36}$$

and then the electric current density as in (2) is also quantized, with n–th value given in dimensionless form by

$$j^{(n)} = [\alpha_-(\theta - \phi) - \alpha_+(\theta + \phi)]/2 - n\theta(\alpha_+ + \alpha_-) \tag{37}$$

and in dimensional form by

$$J^{(n)} = (\hat{z}e)\left[[n + 1 + n(D_-/D_+)]\Phi_+^{(0)} + [n - 1 + n(D_+/D_-)]\Phi_-^{(0)}\right]$$

$$= J^{(0)} + n\Delta J, \quad \Delta J = \tilde{z}e(D_+ + D_-)\left\{\frac{\Phi_+^{(0)}}{D_+} + \frac{\Phi_-^{(0)}}{D_-}\right\}. \tag{38}$$

The case $\theta = 0$ (zero resistive force-density) is degenerate; then ϕ may take any real value, and there is no flux-quantization, as (35) shows. In this case, the system (5) is solvable explicitly in terms of elliptic functions, corresponding to the reduction of PII in (13) to an elliptic ODE [3, 10, 27].

Flux quantization is a remarkable feature of the structure of solutions of (1) when grouped into sequences by Bäcklund transformations. To begin to explore the physical interpretation of this mathematical result, we reconsider Planck's electrically neutral solution (14) in the case $E(x) \equiv 0$ when it becomes an exact solution of (5), that is, when $A_+ = A_- = c_1 - c_0 = A$. We take this as seed solution $\mathcal{S}$ in a doubly-infinite sequence $\mathcal{Q}_{\mathcal{S}}$ of exact

solutions generated by Bäcklund transformations and their inverses. Writing for the moment $\hat{\mathcal{S}} = \mathcal{B}(\mathcal{S})$ and $\mathcal{S}^\dagger = \mathcal{B}^{-1}(\mathcal{S})$ for the two members of this sequence on either side of $\mathcal{S}$, we find using (20) and (21) that $\hat{\mathcal{S}}$ has the form

$$\hat{c}_+(x) = c_0 + Ax + 2\lambda^2 A^2/(c_0 + Ax)^2\,, \quad \hat{c}_-(x) = c_0 + Ax\,,$$

$$\hat{E}(x) = -2A/(c_0 + Ax)\,, \quad \hat{A}_+ = 3A\,, \quad \hat{A}_- = -A\,; \tag{39}$$

$\mathcal{S}$ has the form (from (14))

$$c_+(x) = c_-(x) = c_0 + Ax\,,$$

$$E(x) = 0\,, \quad A_+ = A_- = A\,; \tag{40}$$

and $\mathcal{S}^\dagger$ has the form

$$c_-^\dagger(x) = c_0 + Ax + 2\lambda^2 A^2/(c_0 + Ax)^2\,, \quad c_+^\dagger(x) = c_0 + Ax\,,$$

$$E^\dagger(x) = 2A/(c_0 + Ax)\,, \quad A_+^\dagger = -A\,, \quad A^\dagger = 3A\,. \tag{41}$$

We note that (41) can also be obtained from (39) using (23). In each of these three solutions, the concentrations are everywhere positive as required. It is natural to think of $\mathcal{S}$ as describing a 'ground state' of the system, where $E(x) \equiv 0$ and $j = (\alpha_- - \alpha_+)A$. Then $\hat{\mathcal{S}}$ and $\mathcal{S}^\dagger$ describe 'excited states,' with $j = -(3\alpha_+ + \alpha_-)A$ and $j = (\alpha_+ + 3\alpha_-)A$ respectively. Note however that charge-neutrality at $x = 0$ and $x = 1$ is satisfied by the seed solution $\mathcal{S}$, but not by $\hat{\mathcal{S}}$ and $\mathcal{S}^\dagger$, and it is not clear what interpretation to give to the boundary-values satisfied in these two excited states.

The sequence $\mathcal{Q}_\mathcal{S}$ generated from $\mathcal{S}$ in this case corresponds to the well-known doubly-infinite sequence of rational solutions of PII [18, 19, 21, 22, 10, 11]. Expressions for the members of the sequence beyond those given in (39)-(41) become increasingly more complicated, but it is straightforward to use MATLAB [28] to construct such members approximately without solving (5) numerically, simply by proceeding from the seed solution using (20) and (21).

Fig. 1 shows $c_+(x)$ as in (40) and its first eight iterates under $\mathcal{B}$, for the choices $c_0 = 1/3$, $A = 1/3$, and $\lambda^2 = 0.01$. Note from (20) that these are also the graphs of the first nine iterates under $\mathcal{B}$ of $c_-(x)$, and from (21), they are also the seed and first eight iterates under $\mathcal{B}^{-1}$ of $c_-(x)$, and also the first nine iterates under $\mathcal{B}^{-1}$ of $c_+(x)$. The ninth graph shows unphysical negative concentration values, showing that for these parameter values, there
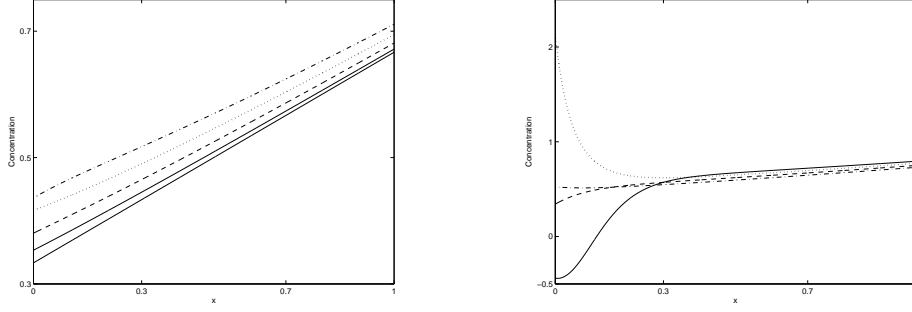
Figure 1: On the left, graphs of $c_+(x)$ (straight, solid) as in (40) and its nth transforms under $\mathcal{B}$, for $n = 1$ (solid), $n = 2$ (dashed), $n = 3$ (dotted) and $n = 4$ (dashdotted). On the right, graphs for $n = 5$ (dashdotted), $n = 6$ (dashed), $n = 7$ (dotted) and $n = 8$ (solid), showing appearance of unphysical negative values in the final case.

is a ground state plus seven excited states plus their seven conjugates. The corresponding evenly-spaced current-density values, from the seventh iterate under $\mathcal{B}^{-1}$ through to the seventh iterate under $\mathcal{B}$ are, in dimensionless and dimensional form

$$j^{(n)} = -[(2n+1)\alpha_+ + (2n-1)\alpha_-]A,$$

$$J^{(n)} = \hat{z}e(c_0 - c_1)[(D_+ - D_-) + 2n(D_+ + D_-)]/\delta,$$

$$n = -7, -6, \cdots, 7. \tag{42}$$

Experiment with this technique using MATLAB shows that the number of excited states with positive concentrations obtained from (14) (in the case with $E(x) \equiv 0$), depends on the values of c_0, c_1 and λ.

Examples like this show that for any physically sensible seed solution $\mathcal{S}$, we must expect that only a finite subsequence of $\mathcal{Q}_\mathcal{S}$ may correspond

to physically meaningful situations; in other words, only a finite number of physically acceptable solutions will be generated from any acceptable seed solution by Bäcklund transformations and their inverses. Within that subset of solutions, however, we have nevertheless the remarkable result that ionic fluxes and the electric current-density are quantized in accordance with (36).

A notable feature of (38) and (42) is that increments of fluxes pertaining to successive values of n are all equal and all determined at $n = 0$, despite radical differences between the solutions of (1) associated with those fluxes at different n values. What common element of such disparate solutions can engender consistency with the equality of the flux increments? We develop elsewhere [29] the hypothesis that the common element is the quantum of electric charge.

[*Remark:* In regard to the general question as to when Bäcklund or inverse Bäcklund transformations of a given physically meaningful solution of (5) give rise to new (potentially) physically meaningful solutions, with positive concentrations, we may make the following intuitive observations. When $D_+ \neq D_-$, it is clear that no steady electric field can counteract diffusion of both ionic species and force both fluxes Φ_+ and Φ_- to zero. However, there is a field capable of equating the fluxes, so that positive and negative ions moving together make up zero electric current density; this is the situation where $J = 0$ in (2). To achieve this, $E(x)$ must be directed so as to oppose the flux of the more mobile species. Because $E(x)$ has to be anti-parallel (resp. parallel) to the flux of positive (resp. negative) ions in order to oppose it, if $D_+ > D_-$ then $E(x)\Phi_+ < 0$, and if $D_+ < D_-$ then $E(x)\Phi_- > 0$. In dimensionless form, if $j = 0$ and $\alpha_+ > \alpha_-$ then $E(x)A_+ > 0$, and if $j = 0$ and $\alpha_+ < \alpha_-$ then $E(x)A_- < 0$. But then it is clear from (20) and (21) that if $c_+(x)$ and $c_-(x)$ are positive, so are their Bäcklund transforms $\hat{c}_+(x)$ and $\hat{c}_-(x)$ in the first case, while their inverse Bäcklund transforms are positive in the second case. Note that this result is independent of the choice of boundary conditions. For $j \neq 0$ the argument breaks down; and since a solution with $j = 0$ is carried by a Bäcklund or inverse Bäcklund transformation into a solution with $j \neq 0$ in general, as (37) shows, the argument cannot be applied more than once to a solution with $j = 0$; then we cannot easily tell if further Bäcklund or inverse Bäcklund transformations will produce solutions with positive concentrations.]

It is clear that an analysis of BCs and positivity requirements for solutions of (5) is called for; we turn to this in the next section.

7 Boundary conditions and positivity of concentrations

The ionic fluxes Φ_+ and Φ_- appearing in (1), and hence the dimensionless constants A_+ and A_- appearing in (5), are not to be considered in general as given. The electric current density (2) and hence the linear combination (6) may be prescribed, but this leaves at least one of A_+ and A_- to be determined as part of any solution $\mathcal{S} = (c_+, c_-, E, A_+, A_-)$ of (5). Five pieces of data must be supplied to fix such a solution.

So far we have partially characterized the seed solution $\mathcal{S}$ of a sequence $\mathcal{Q}_{\mathcal{S}}$ by the values B, θ and ϕ, thus fixing the values of A_+ and A_-. Ignoring for the moment that this may not be possible in practice, we note that the conjugate sequence $\mathcal{Q}_{\mathcal{C}(\mathcal{S})}$ is then also partially characterized, by corresponding values B, θ and $-\phi$, and the reflected sequence $\mathcal{Q}_{\mathcal{R}(\mathcal{S})}$ is also partially characterized, by corresponding values $B - \theta$, $-\theta$ and $-\phi$. Two further numbers are needed to fix each of these three sequences uniquely. They can be taken to be the two further numbers that are needed to fix the seed solution $\mathcal{S} = (c_+, c_-, E, A_+, A_-)$, which so far has, using (9) and (35),

$$A_+ = (\theta + \phi)/2, \quad A_- = (\theta - \phi)/2,$$

$$c_+(0) + c_-(0) - \tfrac{1}{2}\lambda^2 E(0)^2 = B = c_+(1) + c_-(1) - \tfrac{1}{2}\lambda^2 E(1)^2 - \theta. \tag{43}$$

For example, we could prescribe the values at $x = 0$ of all three of c_+, c_- and E, bearing in mind that we have already prescribed the value B of the combination $c_+(0) + c_-(0) - \lambda^2 E(0)^2/2$. Then we can reasonably hope that the seed solution $\mathcal{S}$ is uniquely determined, and so in turn, every element of the sequences $\mathcal{Q}_{\mathcal{S}}$, $\mathcal{Q}_{\mathcal{C}(\mathcal{S})}$ and $\mathcal{Q}_{\mathcal{R}(\mathcal{S})}$.

Writing again $\mathcal{B}^n(\mathcal{S}) = (\hat{c}_+, \hat{c}_-, \hat{E}, \hat{A}_+, \hat{A}_-)$, we could then determine the values of $\hat{c}_+(0)$, $\hat{c}_-(0)$ and $\hat{E}(0)$ by repeated use of the formulas (20) and (21) at $x = 0$, although the resulting expressions quickly become very complicated as $|n|$ increases. Similarly, if we were to fix $\mathcal{S}$ by prescribing the values of $c_+(1)$, $c_-(1)$ and $E(1)$, we could then determine the values of $\hat{c}_+(1)$, $\hat{c}_-(1)$ and $\hat{E}(1)$ by repeated use of the formulas (20) and (21) at $x = 1$. Note however that if we were to fix the seed solution by giving the values of, say, $E(0)$ and $E(1)$ in addition to (43), then we could not determine the values of $\widehat{E}(0)$ and $\widehat{E}(1)$ using (20) and (21) alone.

Because the values of A_+ and A_- are not in general known *a priori*, such considerations are of more mathematical than physical interest, and we now turn to more physically relevant ways of prescribing the five pieces of data needed to fix a solution of (5). Two types of BCs are of particular interest.

7.1 Charge-neutral boundary conditions

These were adopted by Planck [2] and in the formulation of the present model given in [4, 5], and take the form

$$c_+(0) = c_-(0) = c_0 > 0 \text{ and } c_+(1) = c_-(1) = c_1 > 0. \tag{44}$$

Without loss of generality, we can suppose that $c_0 \le c_1$. Taking $c_{ref.}$ to equal the sum of the concentrations at the two faces of the slab before proceeding to dimensionless variables as in (3), we then have in dimensionless form

$$0 < c_0 \le c_1, \quad c_0 + c_1 = 1. \tag{45}$$

Eqs. (44) provide four of the five pieces of data that we expect are needed to determine a solution of (5). The remaining piece is typically provided by fixing the value of the current density,

$$j = j_0. \tag{46}$$

Using the last of (5), we see from (44) that

$$E'(0) = 0 = E'(1), \tag{47}$$

implying Neumann BCs for PII as in (13). However this boundary-value problem for (13) is not of a standard form because constants to be determined as part of the solution appear in the coefficients of the ODE itself. In full, we have using (9), (44) and (46) in (13) that

$$\lambda^2 E''(x) = \tfrac{1}{2}\lambda^2 E(x)^3$$

$$+ \left[2c_0 - \tfrac{1}{2}\lambda^2 E(0)^2 + \left\{ 2(c_1 - c_0) + \tfrac{1}{2}\lambda^2(E(0)^2 - E(1)^2) \right\} x \right] E(x)$$

$$-(\alpha_+ - \alpha_-)\left\{ 2(c_1 - c_0) + \tfrac{1}{2}\lambda^2(E(0)^2 - E(1)^2) \right\} - 2j_0. \tag{48}$$

Here λ, c_0, c_1, α_+, α_- and j_0 are known constants, while $E(0$ and $E(1)$ are to be determined together with $E(x)$, for $0 < x < 1$. Despite its unusual form, in the case $j_0 = 0$ existence of positive, strictly decreasing solutions $E(x)$ of (48) and (47) satisfying $c_0 E(0) < c_1 E(1)$, and non-existence of negative solutions, has been shown [13, 14] for $\alpha_+ > \alpha_-$. By charge-conjugation, existence of negative, strictly increasing solutions satisfying $c_0 E(0) > c_1 E(1)$, and non-existence of positive solutions, has been shown for $\alpha_+ < \alpha_-$. If $\alpha_+ = \alpha_-$, then $j_0 = 0$ implies that $A_+ = A_- = 0$, and the explicit solution $E(x) \equiv 0$ exists as in (14).

From any of these solutions $E(x)$, a solution to (5), (44) and (46) can be constructed using (9) and the last of (5). Note that when $E(x)$ is strictly increasing (resp. decreasing), then $c_+(x) > c_-(x)$ (resp. $c_+(x) < c_-(x)$) on $(0, 1)$.

Uniqueness has not been established for any of these solutions, and there are no general existence or uniqueness results when $j_0 \neq 0$.

It has proved difficult [14] to solve (48) directly by numerical methods in order to obtain approximate solutions that illustrate the results obtained analytically [13, 14]. This difficulty, which stems from the fact that the ODE to be solved involves constants that have to be determined as part of the solution, can be circumvented simply, by working with the system (5) rather than its consequence (48), or more precisely, by rewriting (5) as a system of five coupled first-order ODEs,

$$c_+{}'(x) = E(x)\, c_+(x) + A_+(x)\,, \quad c_-{}'(x) = -E(x)\, c_-(x) + A_-(x)\,,$$

$$\lambda^2 E'(x) = c_+(x) - c_-(x)\,, \quad A_+{}'(x) = 0\,, \quad A_-{}'(x) = 0\,, \tag{49}$$

which does not involve any unknown constants. The MAPLE [15] routine *dsolve* solves (49) almost instantaneously when supplemented by BCs of the form (44) and (46), with the latter rewritten as

$$\alpha_- A_-(0) - \alpha_+ A_+(0) = j_0\,. \tag{50}$$

Fig. 2 shows plots obtained in this way, for $c_0 = 1/3$, $c_1 = 2/3$, $\lambda = 0.5$ and $j_0 = 0$, showing expected behaviour [13, 14]: a positive, monotonically decreasing $E(x)$ on the left, in the case $\alpha_+ = 0.8 > \alpha_- = 0.2$, and a negative, monotonically increasing $E(x)$ on the right in the case $\alpha_+ = 0.4 < \alpha_- = 0.6$. On the left, $c_0 E(0) \approx 0.15 < c_1 E(1) \approx 0.25$; on the right, $c_0 E(0) \approx -0.049 > c_1 E(1) \approx -0.083$. In each case, (47) is satisfied.

Comparison with the behaviour of $E(x)$ in cases with $j_0 \neq 0$, as in Fig. 3 below, suggests strongly that these known existence and monotonicity results [13, 14] can be extended to such cases also.

It is easy to show as follows that for any solution of (5), (44) in which $c_+(x)$ and $c_-(x)$ are continuously once-differentiable on $(0, 1)$, and continuous from the right (resp. from the left) at $x = 0$ (resp. $x = 1$), then both c_+ and c_- are everywhere positive on $[0, 1]$.

Suppose firstly that $c_+(x) < 0$ on some open subinterval of $[0, 1]$. Because $c_+(0) = c_0 > 0$, and $c_+(1) = c_1 > 0$, it then follows that there is at least one point x_1 and one point x_2 in $[0, 1]$ with

$$c_+(x_1) = 0\,, \quad c_+{}'(x_1) \leq 0\,, \quad c_+(x_2) = 0\,, \quad c_+{}'(x_2) \geq 0\,. \tag{51}$$
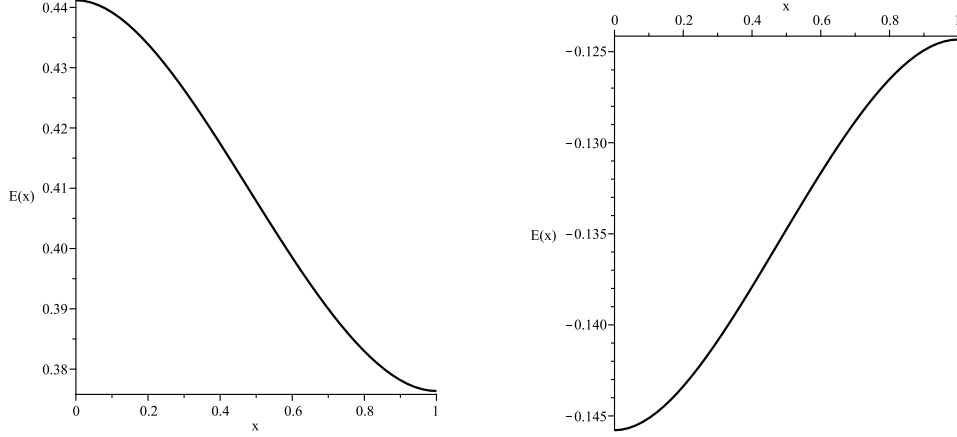
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Figure 2: Graphs of $E(x)$ when $c_0 = 1/3$, $c_1 = 2/3$, $j_0 = 0$ and $\lambda = 0.5$. On the left, $\alpha_+ = 0.8$, $\alpha_- = 0.2$; on the right, $\alpha_+ = 0.4$, $\alpha_- = 0.6$.

These conditions are only compatible with the first of (5) if

$$c_+{}'(x_1) = c_+{}'(x_2) = A_+ = 0\,. \tag{52}$$

But if $A_+ = 0$, it follows from the first of (5) and (44) that

$$c_+(x) = c_0\, e^{\int_0^x E(y)\,dy}\,, \quad 0 \le x \le 1\,, \tag{53}$$

which is everywhere positive, hence providing a contradiction.

Next suppose instead that $c_+(x_3) = 0$ at some point $x_3 \in [0, 1]$. Because it cannot happen that $c_+(x) < 0$ on an open subinterval of $[0, 1]$, it follows that x_3 is a minimum, and $c_+{}'(x_3) = 0$, so again from the first of (5) we have $A_+ = 0$, hence (53), and again a contradiction.

Thus $c_+ > 0$ on $[0, 1]$, and similarly $c_- > 0$ on $[0, 1]$.

With that established, it is possible to prove for any solution of this type that at least one of A_+ and A_- must be positive if $c_1 > c_0$. Assume to the contrary that $A_+ \le 0$ and $A_- \le 0$. From (5) it then follows that

$$d\left(e^{\psi(x)}\, c_+(x)\right)/dx = A_+\, e^{\psi(x)} \le 0\,,$$

$$d\left(e^{-\psi(x)}\, c_-(x)\right)/dx = A_-\, e^{-\psi(x)} \le 0\,, \tag{54}$$
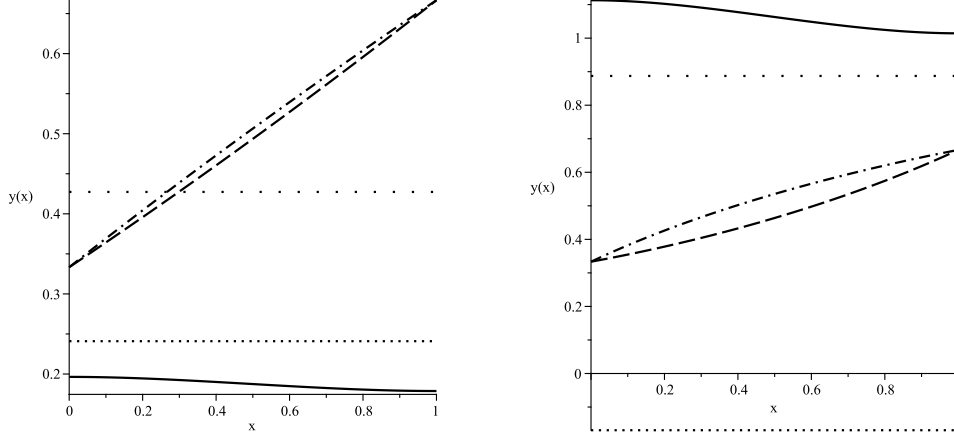
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Figure 3: Graphs of $c_+(x)$ (dash), $c_-(x)$ (dashdot), $E(x)$ (solid), A_+ (dot) and A_- (spacedot), corresponding to charge-neutral BCs (44), (46), with $c_0 = 1/3$, $c_1 = 2/3$, $\lambda = 0.7$, $\alpha_+ = 0.4$, $\alpha_- = 0.6$ in each case, and with $j_0 = 0.16$ on the left, and $j_0 = 0.6$ on the right. Both A_+ and A_- are positive on the left; on the right, A_- is positive but A_+ is negative.

where

$$\psi(x) = -\int_0^x E(y)\,dy\,. \tag{55}$$

Then

$$e^{\psi(0)}\,c_+(0) \geq e^{\psi(1)}\,c_+(1) \Rightarrow e^{\psi(0)-\psi(1)} \geq c_1/c_0\,,$$

$$e^{-\psi(0)}\,c_-(0) \geq e^{-\psi(1)}\,c_-(1) \Rightarrow e^{\psi(0)-\psi(1)} \leq c_0/c_1\,, \tag{56}$$

which are inconsistent with $c_1 > c_0$.

Numerical experiments indicate that there are cases for which both of A_+, A_- are positive, and cases where only one is positive. Fig. 3, obtained in the same way as Fig. 2 above, shows examples of both behaviours. Note that if $j_0 = 0$ in (46), then (7) implies that A_+ and A_- have the same sign, and so both must be positive if $c_1 > c_0$.

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We now show that BCs of the form (44) and (45) are not preserved under Bäcklund transformations. We have already seen this in the special case of the exact Planck solution, described in (14). Consider $\hat{\mathcal{S}} = \mathcal{B}(\mathcal{S})$ where $\mathcal{S}$ is a solution satisfying (44) for some c_0 and c_1 as in (45). From (20) we see that $\hat{c}_+(0) = \hat{c}_-(0)$ requires that

$$2A_+\lambda^2(c_0 E(0) + A_+)/c_0^2 = 0 \,, \tag{57}$$

which in turn requires either $A_+ = 0$ or $c_+{}'(0) \ (= c_0 E(0) + A_+) = 0$. Similarly, either $A_+ = 0$ or $c_+{}'(1) = 0$. But since $\mathcal{S}$ should be fixed by the five pieces of data in (44) and (46), it is not possible to *impose* any of these conditions, and none will hold in general. Certainly there can be solutions $\mathcal{S}$ for which (44) hold together with $A_+ = 0$ rather than (46), but then the corresponding current-density j is not known *a priori*, but is determined as part of the solution. In such a case, $\mathcal{B}(\mathcal{S})$ reduces to $\mathcal{C}(\mathcal{S})$, the charge-conjugate of $\mathcal{S}$, with $\hat{A}_+ = A_-$ and $\hat{A}_- = 0$, as noted after (20). It follows that a second iteration of $\mathcal{B}$ is not possible unless it is also true that $A_- = 0$; but when $A_+ = A_- = 0$, no flux-quantization occurs, as (36) shows. Corresponding remarks apply for inverse Bäcklund transformations. Thus charge-neutral BCs (44) are not preserved in form under flux-quantization by Bäcklund transformations and their inverses.

7.2   Corrected boundary conditions

In proposing charge-neutral BCs (44), we have in mind reservoirs of well-stirred ionic solutions occupying $-\infty < x < 0$ and $1 < x < \infty$, with $c_+(x)$ and $c_-(x)$ both equal to c_0 throughout the left-hand reservoir, and both equal to c_1 throughout the right-hand reservoir, and with $E(x) = 0$ throughout both reservoirs. Stirring leads to the diffusion coefficients D_+ and D_- becoming effectively infinite, so that we also have $A_+ = A_- = j = 0$ throughout both reservoirs (*cf.* (1) and (5)). When, as we expect, (44) and (46) determine a solution of (5) in $0 < x < 1$, boundary-values $E(0_+)$ and $E(1_-)$ of $E(x)$ are determined in turn as part of that solution. There is no reason to expect that these values will be zero in general, and so they will not equal the assumed values in the reservoirs, $E(0_-) = E(1_+) = 0$. But such jumps in the values of $E(x)$ across the faces of the slab imply the presence of nonzero surface charges, contradicting the assumption of charge neutrality there. From this point of view, the charge-neutral BCs (44) are inconsistent.

   In reality, we must expect that the ionic concentrations and the electric field are continuous across each face of the slab. Then, for the left-hand reservoir for example, $c_+(0) \neq c_-(0)$ and $E(0) \neq 0$, but as $x \to -\infty$, $c_+(x)$

and $c_-(x)$ decay to a common positive value $c_{(-\infty)}$, while $E(x)$ decays to zero. Similarly, in the right-hand reservoir as $x \to \infty$, $c_+(x)$ and $c_-(x)$ decay to a common positive value $c_{(+\infty)}$, while $E(x)$ decays to zero. Without loss of generality, we can suppose that $c_{(+\infty)} \geq c_{(-\infty)}$. It is now appropriate to choose the sum of these two limiting concentrations, before the change to dimensionless variables, as the c_{ref} in (3) and (4); in dimensionless terms we then have in place of (45) that

$$0 < c_{(-\infty)} \leq c_{(+\infty)}, \quad c_{(-\infty)} + c_{(+\infty)} = 1. \tag{58}$$

In the left-hand reservoir, equations of the form (1) apply in simplified form, as $D_+ \to \infty$ and $D_- \to \infty$; in dimensionless form, we get equations of the form (5) with $A_+ = A_- = 0$, so that for $-\infty < x < 0$ we have to solve

$$c_+{}'(x) = E(x)c_+(x), \quad c_-{}'(x) = -E(x)c_-(x),$$

$$\lambda^2 E'(x) = c_+(x) - c_-(x), \tag{59}$$

with $c_\pm(x) \to c_{(-\infty)}$ and $E(x) \to 0$ as $x \to -\infty$. Then the first two equations integrate to

$$c_+(x) = c_{(-\infty)}\, e^{-\varphi(x)}, \quad c_-(x) = c_{(-\infty)}\, e^{\varphi(x)}, \tag{60}$$

where

$$\varphi(x) = -\int_{-\infty}^{x} E(x)\,dx \tag{61}$$

is the electrostatic potential of the electric field in the reservoir. Because $E(x) = -\varphi'(x)$, the third of (59) then gives the nonlinear Poisson-Boltzmann equation

$$-\lambda^2 \varphi''(x) = c_{(-\infty)} \left[e^{-\varphi(x)} - e^{\varphi(x)} \right], \tag{62}$$

to be solved on $-\infty < x < 0$ subject to $\varphi(x) \to 0$ and $\varphi'(x) \to 0$ as $x \to -\infty$. The exact solution of this problem is known [30, 31]. In Appendix B we present this solution and describe the highly nonlinear exact BCs at the junction face(s) to which it leads. Here we suppose that

$$|\varphi(x)| \ll 1, \tag{63}$$

so that (62) linearizes to

$$\lambda_0^2\, \varphi''(x) = \varphi(x), \quad \lambda_0 = \lambda/\sqrt{2c_{(-\infty)}}. \tag{64}$$

with solution matching the limiting BCs at $x = -\infty$ given by

$$\varphi(x) = \varphi(0)\, e^{x/\lambda_0}\,. \tag{65}$$

In this approximation we then have, from (60) and (61),

$$c_+(x) = c_{(-\infty)} \left[1 - \varphi(0)\, e^{x/\lambda_0} \right]\,,$$

$$c_-(x) = c_{(-\infty)} \left[1 + \varphi(0)\, e^{x/\lambda_0} \right]\,,$$

$$E(x) = -\frac{\varphi(0)}{\lambda_0}\, e^{x/\lambda_0}\,, \tag{66}$$

showing that λ_0 (in dimensional form, $\lambda_0 \delta$) can be interpreted as a Debye shielding length for the reservoir-junction interface. It is the characteristic length over which $c_+(x)$, $c_-(x)$ and $E(x)$ decay to their limiting values as x decreases from the interface value $x = 0$. In terms of the original variables,

$$\lambda_0 \delta = \sqrt{\epsilon k_B T / 8\pi (\tilde{z}e)^2 c_{(-\infty)}}\,. \tag{67}$$

[*Remark:* Just as λ_0 is a Debye length at concentration $c_{-\infty}$, so the constant $\lambda/\sqrt{2}$ of (4) is a Debye length at concentration $c_{ref.}$. In analyzing mathematically situations where λ approaches zero [32] (see Sec. 3), a different choice of $c_{ref.}$ in (4) may be more appropriate than the one we have made at the start of this section. For example the choice of the logarithmic mean $(c_{(+\infty)} - c_{(-\infty)})/\ln(c_{(+\infty)}/c_{(-\infty)})$ as $c_{ref.}$ has the advantage that $c_{ref.}$ then tends to zero like the smaller of $c_{(-\infty)}$ and $c_{(+\infty)}$, guaranteeing that as λ approaches zero, the Debye length in each reservoir also approaches zero.]

In (66), the value of $\varphi(0)$ is determined from the solution of (5) in the slab, which fixes $c_\pm(0)$ and $E(0)$.

From (66) we have

$$c_+(0) + c_-(0) = 2c_{(-\infty)}\,,$$

$$c_+(0) - c_-(0) = -2c_{(-\infty)}\varphi(0) = 2c_{(-\infty)}\lambda_0 E(0)\,, \tag{68}$$

and then, from the third of equations (59),

$$\lambda_0 E'(0) = E(0)\,. \tag{69}$$

Similar considerations in the right-hand reservoir lead to

$$c_+(1) + c_-(1) = 2c_{(+\infty)}\,,$$

$$c_+(1) - c_-(1) = 2c_{(+\infty)}\lambda_1 E(1)\,, \tag{70}$$

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and

$$\lambda_1 E'(1) = E(1). \tag{71}$$

In (70) and (71), λ_1 is defined like λ_0 in (64), with $c_{(+\infty)}$ replacing $c_{(-\infty)}$.

With $c_{(-\infty)}$, $c_{(+\infty)}$ and j_0 given constants, equations (68), (70) and (46) provide the new BCs that are to be applied to fix a solution of the system (5) on $0 < x < 1$, replacing (44) and (46). Fig. 4 provides an illustration of the solution to the combined problem (left reservoir, slab, right reservoir). In the slab, equations (5) were solved numerically using MAPLE, with the BCs (68) and (70).
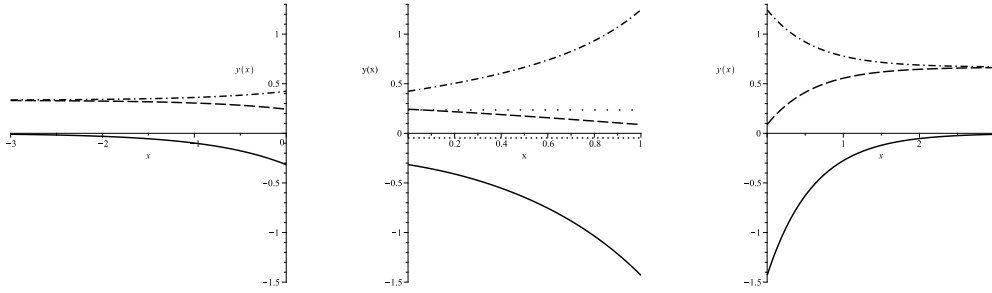

Figure 4: Graphs of $c_+(x)$ (dash), $c_-(x)$ (dashdot), $E(x)$ (solid), A_+ (dot) and A_- (spacedot), in the left reservoir, in the slab, and in the right reservoir, corresponding to corrected (approximate) BCs. Parameter values are $c_{(-\infty)} = 1/3$, $c_{(+\infty)} = 2/3$, $\lambda = 0.7$, $\alpha_+ = 0.4$, $\alpha_- = 0.6$, with $j_0 = 0.16$.

This boundary value problem can also be posed in terms of PII, which in this case takes a simpler, more standard form than (48). To see this, note firstly that c_0 and c_1 in (48) are now to be replaced by $c_{(-\infty)}$ and $c_{(+\infty)}$, respectively, according to the first of (68) and the first of (70). Then note that, as a consequence of (63) and the third of (66),

$$\tfrac{1}{2}\lambda^2 E(0)^2 \ll 2c_{(-\infty)}. \tag{72}$$

Similarly

$$\tfrac{1}{2}\lambda_1^2 E(1)^2 \ll c_{(+\infty)}. \tag{73}$$

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The terms on the left-hand sides of these inequalities are therefore to be neglected relative to the terms on the right-hand sides in the ODE that replaces (48), and it therefore takes the form

$$\lambda^2\, E''(x) = \tfrac{1}{2}\lambda^2 E(x)^3 + 2\left[c_{(-\infty)} + \left\{c_{(+\infty)} - c_{(-\infty)}\right\} x\right] E(x)$$

$$-2(\alpha_+ - \alpha_-)\left\{c_{(+\infty)} - c_{(-\infty)}\right\} - 2j_0\,. \qquad (74)$$

This equation is to be solved on $0 < x < 1$, subject to the radiation BCs (69) and (71). The constants $c_{(-\infty)}$, $c_{(+\infty)}$, α_+, α_- and j_0 appearing here are to be regarded as given. Nothing is known about existence or uniqueness of solutions to this problem, to our knowledge, nor about positivity of resultant concentrations.

Given (72) and (73), the question arises if $\tfrac{1}{2}\lambda^2 E(x)^2$ should also be neglected relative to $c_{(-\infty)}$ and $c_{(+\infty)}$ for all $0 < x < 1$, and not only at the boundaries. If so, then the cubic term in (74) drops out, and the resultant linear boundary-value problem should be exactly solvable in terms of Airy functions (*cf.* [5]). This will not be pursued here.

Similar manipulations to those in the preceding subsection show that, like charge-neutral BCs, those in (68), (70) and (46) are also not preserved in form under Bäcklund transformations and their inverses.

8   Concluding remarks

Quantization of ionic fluxes and of the electric current-density by Bäcklund transformations of solutions, in this one-dimensional model of electrodiffusion within a liquid junction, is a remarkable mathematical phenomenon. What physical significance can be attached to this phenomenon is not completely clear, but the example provided by the exact Planck solution and its transforms is highly suggestive of a corresponding ground state and excited states of the system. A difficulty with this interpretation, and with the concept of flux-quantization by Bäcklund transformations more generally, is that BCs that are invariant in form under such transformations have not yet been identified.

We have seen that familiar charge-neutral BCs, first introduced in the context of electro-diffusion by Planck, lead to several attractive properties of solutions. Existence of such solutions has previously been proved under certain conditions [13, 14], and we have shown positivity of the functions representing ionic concentrations. However, we have argued that such BCs are not physically consistent. Moreover, they are not preserved in form under

Bäcklund transformations. This has prompted us to examine more realistic BCs. To find these we have had to solve for the exact form of ionic concentrations and the electric field in well-stirred reservoirs outside each face of the junction. The new BCs define novel boundary-value problems for the system of ODEs that determine the model of electrodiffusion in the junction. A physically sensible approximation to these reservoir solutions has been found to lead to radiation BCs for the Painlevé II ODE which lies at the heart of the model, while the exact solutions lead to highly nonlinear BCs for that ODE.

These new BCs, either exact or approximate, are not preserved in form under Bäcklund transformations, and it remains to classify BCs, as generated by such transformations, that are physically relevant. The application of Bäcklund transformations to link boundary value problems of physical relevance does arise elsewhere, in particular in elasticity [12]. There mixed boundary value problems associated with normal loading and application of torsion may be linked in that way. Further applications involve boundary value problems describing indentation of shear-strained nonlinear elastic materials [33]. We can be optimistic, therefore, that Bäcklund transformations can also be shown to relate physically interesting BCs in the present context.

We have shown for the present model that Bäcklund transformations do leave invariant two quantities. One represents the total ionic (osmotic) pressure within the junction. The other represents the total resistive force per unit volume that the solute offers against ionic transport. We may hope that the invariance of these quantities provides a clue in the ongoing study of BCs and their relationship to flux-quantization by Bäcklund transformations.

Appendix A: Gambier transformations of exact solutions

Consider again the exact case of Planck's solution, as in (40). Note that for this solution, B as in (9) takes the value $2c_0$, and $A_+ = A_- = A$, as required for application of $\mathcal{G}_+^{-1}$. We consider a small perturbation of this solution in the form

$$c_\pm(x) = c_0 + Ax + \epsilon\, d_\pm(x)\,, \quad E(x) = \epsilon\, F(x)\,, \quad A_\pm = A\,, \qquad \text{(A1)}$$

where $d_\pm(x)$ and $F(x)$ are to be determined by requiring that $c_\pm(x)$, $E(x)$ and $A_\pm$ satisfy (5) to first-order in ϵ, given that they satisfy the system to zeroth-order because (40) is already a solution. Substituting from (A1) into

(5) gives at first-order

$$d_+{}'(x) = (c_0 + Ax)\,F(x)\,, \quad d_-{}'(x) = -(c_0 + Ax)\,F(x)\,,$$

$$\lambda^2 F'(x) = d_+(x) - d_-(x)\,, \tag{A2}$$

and hence

$$\lambda^2 F''(x) = 2(c_0 + Ax)\,F(x)\,. \tag{A3}$$

This has the general solution

$$F(x) = a\mathrm{Ai}(s) + b\mathrm{Bi}(s)\,, \quad s = 2(c_0 + Ax)/(4\lambda^2 A^2)^{1/3} \tag{A4}$$

where Ai and Bi are Airy functions of the first and second kind [34], and a, b are arbitrary constants. Substituting from (A1) into (26) after noting that

$$
\begin{aligned}
c_+(x) - c_-(x) &= \epsilon[d_+(x) - d_-(x)] \\[2mm]
&= \epsilon\lambda^2 F'(x) \\[2mm]
&= \epsilon(J\lambda^4)^{1/3}[a\mathrm{Ai}'(s) + b\mathrm{Bi}'(s)\,, \tag{A5}
\end{aligned}
$$

and then letting $\epsilon \to 0$, we obtain the new solution

$$\hat{c}_+(x) = 0\,, \quad \hat{c}_-(x) = 2\lambda^2 F'(x)^2/F(x)^2 - 4Ax - 4c_0$$

$$\hat{E}(x) = 2F'(x)/F(x)\,, \quad \hat{A}_+ = 0\,, \quad \hat{A}_- = -4A\,, \quad \hat{B} = -4c_0\,, \tag{A6}$$

with F and F' as in (A4) and (A5). The treatment of $\mathcal{G}_-^{-1}$, from the same starting point, is similar, and leads to the conjugate solution to (A6), as follows from (28). It is easily checked also that, just as the inverse Gambier transformations carry the seed solution (40) for the sequence of exact rational solutions of PII into the seed solution for the sequence of exact Airy solutions, so the Gambier transformations $\mathcal{G}_\pm$ carry the seed solutions for these Airy sequences, namely (A6) and its conjugate, back into the seed solution (40) for the sequence of rational solutions.

Remark: These calculations reveal, for the first time, a connection between the approximate solution [5] of PII in terms of Airy functions, and the known sequences of exact solutions of PII in terms of Airy functions [11]. The former is essentially $E(x)$ as in (A1), (A4), while the latter are generated from (A6) and its conjugate by Bäcklund transformations.

Appendix B: Exact boundary conditions and reservoir solutions

The exact solution of (62), with the behaviour at $x = -\infty$ described there, is known to be [30, 31]

$$\varphi(x) = 2\ln\left[\left(1 + Ae^{x/\lambda_0}\right)/\left(1 - Ae^{x/\lambda_0}\right)\right], \quad -1 < A < 1, \quad \text{(B1)}$$

where λ_0 is as in (64). From (60) and (61) we then get

$$c_+(x) = c_{(-\infty)}\left[\left(1 - Ae^{x/\lambda_0}\right)/\left(1 + Ae^{x/\lambda_0}\right)\right]^2,$$

$$c_-(x) = c_{(-\infty)}\left[\left(1 + Ae^{x/\lambda_0}\right)/\left(1 - Ae^{x/\lambda_0}\right)\right]^2,$$

$$E(x) = -4Ae^{x/\lambda_0}/\lambda_0\left(1 - A^2 e^{2x/\lambda_0}\right). \quad \text{(B2)}$$

throughout the left-hand reservoir. The approximations are recovered when $\exp(x/\lambda_0) \ll 1$, so that (66) hold as before.

From (B2) we have in particular that

$$c_+(0) = c_{(-\infty)}\,(1 - A)^2/(1 + A)^2,$$

$$c_-(0) = c_{(-\infty)}\,(1 + A)^2/(1 - A)^2,$$

$$E(0) = -4A/\lambda_0(1 - A^2), \quad \text{(B3)}$$

from which we get

$$c_+(0)c_-(0) = c_{(-\infty)}{}^2, \quad \lambda_0 E(0) = \sqrt{2c_+(0)} - \sqrt{2c_-(0)}. \quad \text{(B4)}$$

These are the nonlinear exact BCs that now apply at the left-hand reservoir-junction interface when solving (5). Similarly, at the right-hand interface we get

$$c_+(1)c_-(1) = c_{(+\infty)}{}^2, \quad \lambda_1 E(1) = \sqrt{2c_+(1)} - \sqrt{2c_-(1)}. \quad \text{(B5)}$$

With a little effort it can be seen that the conditions (B4) and (B5) can also be written in the form

$$c_\pm(0) = c_{(-\infty)} + \tfrac{1}{4}\lambda^2 E(0)^2 \pm \tfrac{1}{4}\lambda E(0)\sqrt{8c_{(-\infty)} + \lambda^2 E(0)^2},$$

$$c_\pm(1) = c_{(+\infty)} + \tfrac{1}{4}\lambda^2 E(1)^2 \pm \tfrac{1}{4}\lambda E(1)\sqrt{8c_{(+\infty)} + \lambda^2 E(1)^2}, \quad \text{(B6)}$$

from which the approximate forms (66) are easily recovered.

The nonlinear BCs that apply for PII in the slab in this case can be seen from (B6); nothing is known about existence or uniqueness of its solutions.

Once again it can be checked that BCs of the form (B6) are not preserved during flux-quantization by Bäcklund transformations.

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